

FINAL REPORT

MEMS Sensors with Chemically
Selective Coatings of Ionic Liquids

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Strategic Environmental Research and
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Nuclear Science and Technology Division

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OF IONIC LIQUIDS**

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ACRONYMS

DoD	U.S. Department of Defense
MC	Microcantilever
MEMS	Micro-electro-mechanical-systems
PSD	Position-sensitive detector
SEED	SERDP Exploratory Development
SERDP	Strategic Environmental Research and Development Program
SON	Statement of needs

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EXECUTIVE SUMMARY

This Strategic Environmental Research and Development Program (SERDP) Exploratory Development (SEED) project is focused on the use of ionic liquids as coatings for microcantilever transducers with the objective to achieve selective detection of air- and water-quality parameters through microelectromechanical systems (MEMS)-based sensors. Ionic liquids offer advantages of stability due to extremely low vapor pressure and selective uptake of analytes from the atmosphere or from aqueous solutions. Methods have been devised to reproducibly apply a coating of a selected ionic liquid on the surface of a microcantilever transducer and test the response of the cantilever in terms of bending and/or changes in oscillation frequency. Through a calibration procedure, the response can be translated into concentration of the analyte, and from the responses of arrays of microcantilevers, the concentration of mixtures can be determined. In this work, the goal was to demonstrate the principle that ionic liquids can be used as coatings for MEMS sensors. To achieve this goal, we first identified the desired properties of ionic liquids for this application. Then, a method was developed to apply coatings of the selected ionic liquid on the microcantilevers. The response of coated cantilevers was tested for various vapor analytes, including water, acetone, and ethanol. The results of these tests were encouraging and led to subsequent measurements with real atmospheric contaminants such as NO_x , ozone, and CO_2 . Response measurements of vapor analytes at high temperatures, as well as for particles in aqueous solutions, were also obtained. The results of this SEED project have shown that ionic-liquid coatings generate desirable response for microcantilevers and may be suitable for use in detection of vapor and aqueous analytes. Furthermore, they are stable in various environments, including atmospheric conditions and high-temperature vapors. Their performance makes them very good candidates for MEMS-based sensor applications. Future work should be focused on the selection of ionic liquids for specific analytes and the development of an integrated MEMS sensor with arrays of microcantilevers.

ABSTRACT

Ionic-liquid-coated cantilevers were used in this study to investigate their response to gaseous and aqueous analytes. A coating method has been developed to ensure that the cantilevers are uniformly coated. It was found that higher-viscosity ionic liquids helped to achieve a uniform coating. Furthermore, addition of nanoparticles and fabrication of nanostructures on the surface of microcantilevers were found to increase the uniformity of the ionic-liquid coatings. Deflection and oscillation frequency-shift measurements were obtained for various vapor analytes including water, ethanol, acetone, carbon dioxide, ozone, and nitrous oxides in single-analyte tests. All analytes but ozone showed a strong, reproducible response, indicating a potential for ionic-liquid use in microcantilever-based detection devices. This does not mean that ozone cannot be detected by ionic-liquid-coated microcantilevers. A systematic study of ionic-liquid properties can reveal better candidates for ozone detection than the ionic liquid selected in this study. Response measurements of particles and dissolved analytes in aqueous solutions were more complex than in gaseous systems. This means that the interpretation of the results in terms of the origin of the response will be difficult. However, the coated microcantilever appeared to be sensitive to the Brownian motion of the particles in the suspension and thus could potentially serve as a detector for similarly sized, nonbenign waterborne particles introduced into the environment. The main conclusion of this Strategic Environmental Research and Development Program (SERDP) Exploratory Development (SEED) project is that because of their favorable physical and chemical properties, ionic liquids are in general good candidates for further investigation for use as coatings of microcantilevers, which are critical parts of microelectromechanical systems sensors. The ionic liquids appear to increase the sensitivity of the response of the cantilevers to airborne contaminants.

1. PROJECT OBJECTIVE

A SEED statement of needs (SON) with the number CPSEED-06-01, issued in November 2004, is focused on the development of miniature sensors for monitoring environmental parameters, including water-quality parameters (e.g., dissolved O₂ and turbidity), waterborne pollutants (e.g., metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls), air-quality parameters (e.g., NO_x, SO_x, ozone, particulates). CPSEED-06-01 states that it is desirable that the sensors have long lifetimes in the field and be able to report measurements remotely, as well as produce accurate and repeatable data. The development of small or miniature instruments (e.g., micro- or nanotechnologies) is encouraged in order to provide small-instrument-package profiles for use in the field. The technologies that are developed and tested should be innovative and be able to withstand environmental extremes as well as possible disruption due to military activities.

In order to satisfy this SEED SON, the objective of this project was to investigate whether ionic liquids could be used as coatings for microcantilevers (MCs) used in microelectromechanical systems (MEMS)-based detectors of air- and water-quality parameters. Several water-quality parameters (latex particles and ethanol) and air-quality parameters (ozone, CO₂, and NO_x) were identified for detection by ionic-liquid-coated MC sensors. The same responses were measured after a period of several days to ensure the reproducibility or long lifetimes of the sensor. In addition, heat was applied to the system to simulate an extreme environment and the signal was detected in order to demonstrate the stability and sensitivity of the sensor when the system is under an extreme environment of high temperature.

2. BACKGROUND

In recent years, microcantilevers (MCs) have been explored—for their role as physical transducers in chemical, physical, and biological sensing systems—as part of MEMS to detect gas- or liquid-phase species [1-4]. Some of these activities can be military related, such as disturbances in and around stream and riparian areas due to tank and vehicle crossing. Air-quality monitoring has long been a subject of research that seeks new means to observe the present conditions as well as changes over time. Some air-monitoring devices are used in smoke or incinerator stacks to allow assessment of the flue gas and particles in order to meet strict air-quality regulations. Different monitoring devices as required for keeping track of volatile materials used in a wide variety of remanufacturing and repair undertaken by the U.S. Department of Defense (DoD) in the maintenance of its weaponry and support equipment.

MCs respond to environmental stimuli, such as gaseous contaminants in the atmosphere or dissolved contaminants in liquids. These stimuli affect the micromechanical characteristics of the transducers, which can be monitored using optical, electronic, or other means. The response of MCs is related to changes in their physicochemical properties such as mass, resonance frequency, and energy content. Changes in the intrinsic stress and loaded mass of the MC that result from interfacial processes (i.e., sorption and desorption) lead to direct, highly sensitive, and rapid detection of chemical analytes. As the size of MCs becomes smaller, their mechanical reaction may begin to share similarities with the vibrational mode of molecules [3,4].

The responses of MCs, which are representative of the micromechanical characteristics of the cantilevers, can be measured in several ways. For example, changes in the loaded mass of cantilevers result from the uptake of chemical species present in the environment. Changes in surface area or mass loading on the MC surface can modulate surface stress because of the thin geometry of MCs, which leads to extremely high surface-to-volume ratios. If the external gravitational, magnetic, and electrostatic forces are negligibly small, the gradient of mechanical stress between the two sides of a cantilever is the only significant factor in cantilever deformation. The MC tip displacement, Δz , resulting from differential stress on its opposite sides can be described by the differential stress

$$\text{Stoney equation: } \Delta z = \frac{1}{2} \frac{l^2}{R} = \frac{3l^2(1-\nu)}{Et^2} \Delta\sigma, \text{ where } l, R, \text{ and } t \text{ are, respectively, the length, radius}$$

of curvature, and thickness of the cantilever; ν and E are Poisson's ratio and Young's modulus for the substrate, respectively; and $\Delta\sigma$ is the differential surface stress [1].

In this study, the effect of a coating of ionic liquid was investigated as a means to enhance the differential stress on the cantilever. Also, the modulated surface stress can change the resonance frequency of MCs. The resonance frequency of the mechanical resonator can be described by

$$f_{0,Q} = \frac{1}{2^{3/2} \pi} \sqrt{\frac{k}{m_0}} \frac{\sqrt{2Q-1}}{Q}, \text{ where } k \text{ is a spring constant of the cantilever; } m_0 \text{ is an effective}$$

suspended mass; and Q is a mechanical quality factor that is inversely proportional to the damping coefficient, defined as $Q = \frac{2\pi W_0}{\Delta W}$. Here, W_0 and ΔW are the accumulated and dissipated mechanical

energy per vibration cycle, respectively [1]. A resonance-frequency shift resulting from the interaction of MCs with their environment may be caused by several mechanisms: for example, adsorbate-induced mass loading (m_0), chemically induced changes in the cantilever stiffness (k), and mechanical damping by the viscous medium (Q).

Several published reports confirm that MC-based sensors with a thin solid film (e.g., gold film) are applicable for detection of specific chemicals [2,5-7]. Efforts have also been made to increase the magnitude of the signal, because the surface stress of a smooth cantilever surface is relatively small.

Cantilevers with nanostructured surfaces or grooved-surface cantilevers showed enhanced output signals [6, 7]. For instance, grooves on cantilevers reduce stress-induced slippage of the film, thus leading to enhanced detection sensitivity of MCs. This work has demonstrated that liquid-phase coatings can replace solid-phase chemical treatment as chemical sensors for gas-phase analytes. Ionic liquids were chosen as coating materials because they are in liquid state at room temperature and hence are easily applied to the cantilever.

MCs used as chemical sensors bend as a result of the difference in surface stresses between the two sides of the asymmetric cantilevers. One side of an asymmetric MC was coated with a thin chemical film of ionic liquid that sorbs target analytes, and the other side was clean. The surface energy of the chemically treated side changed as a result of the interaction of contaminants with ionic liquid, while the opposite side of the cantilever was expected to be passive. The bending of a cantilever and its resonance-frequency shift resulting from sorption or desorption of a target analyte were monitored using a position-sensitive photodetector (PSD). A laser beam was focused onto the cantilever tip, and the position of the reflected spot was monitored by the PSD (see Fig. 1). Resonance frequency and cantilever deflection, among other MC responses to vapors of volatile chemicals, were investigated.

Analytes were introduced via a syringe into a flow cell where the cantilever was located. Acetone, ethanol, or water vapors were produced from injection of the pure liquid-phase chemicals in the syringe. All analytes were introduced into the cell with nitrogen gas flow.

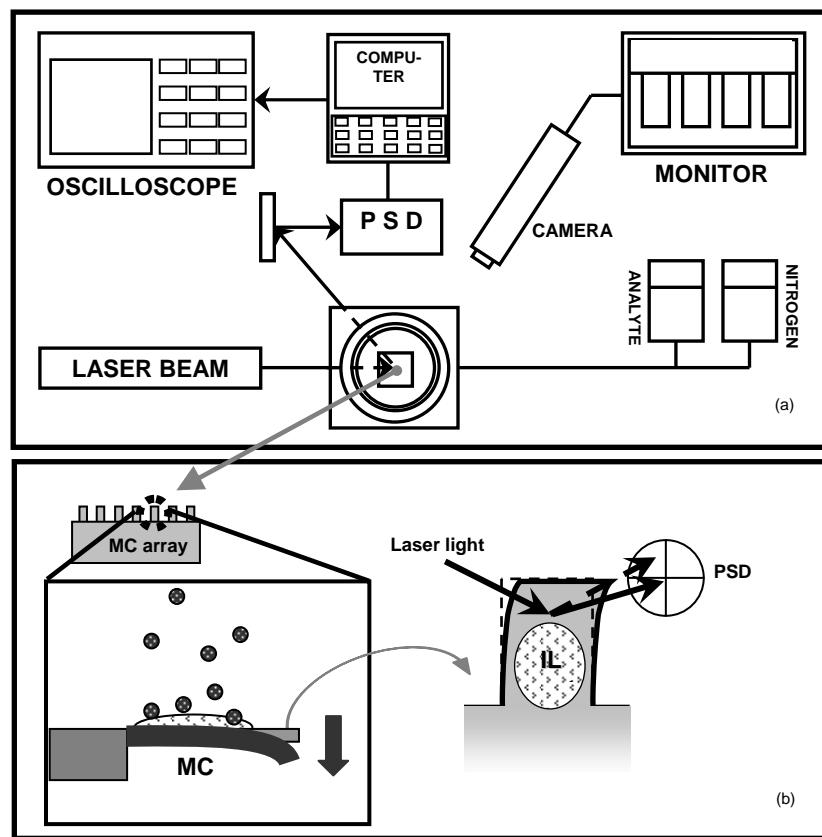


Fig. 1. Analyte delivery system, showing microcantilever deflection. (a) Schematic representation of the analyte delivery system, consisting of an analyte-containing syringe and a nitrogen gas tank. (b) Illustration of MC deflection due to analyte sorption or desorption by the ionic-liquid coating. A laser beam is focused on the cantilever tip, and the position movement of the reflected spot is monitored via a position-sensitive detector (PSD). The PSD is connected to an oscilloscope for direct observation of the signal and to a computer for data acquisition. The recorded PSD output (in Volts) is used as a measure of the MC deflection.

3. IDENTIFICATION OF IONIC LIQUIDS SUITABLE FOR MC COATINGS

Ionic liquids are composed entirely of ions, similar to the ionic melts that can be produced when normal metallic salts are heated [8-10]. Because of their extremely low vapor pressure, ionic liquids constitute a new class of materials that can be used as room temperature solvents in chemical separations and catalysis applications. Some ionic liquids have characteristics that could prove favorable for use in sensors: for example, air and water stability (i.e., extremely low vapor pressure and solubility), wide liquidus range, and relatively favorable viscosity or density characteristics [8,10,11]. Depending on the physical phenomenon involved, a coating of ionic liquid can swell or shrink. For example, sorption of analytes by an ionic liquid may cause swelling of the coating; likewise, desorption may cause shrinking. Such characteristics make these ionic liquids suitable for detection of analytes in liquid or atmospheric environments via MEMS [12]. Some ionic liquids also have strong affinities for selected chemical species. Sensors comprising multiple MCs, each with a different ionic liquid coating can not only detect targeted analytes but also help identify chemical speciation.

The ionic liquid used in this work which has a sulfonate anion is P_{666,14} LABs (triethyltetradecylphosphonium dodecylbenzenesulfonate) obtained from Rex Ren (Wesleyan University, Connecticut). This is a relatively water-insoluble ionic liquid that has high viscosity at room temperature [10,11], stability in water and in the atmosphere, and extremely low vapor pressure. These characteristics make its use in detecting both gaseous and liquid contaminants possible. Its high viscosity helps to stabilize the ionic-liquid coating on one of the two sides of the cantilever.

4. MEASUREMENTS OF AIR-QUALITY PARAMETERS

4.1 PREPARATION OF IONIC-LIQUID-COATED MCs

Commercially available silicon MCs obtained from MikroMasch Co. (<http://mikromasch.com/>), Sunnyvale, California (a U.S. distributor) were used in this study. The cantilevers are rectangular in shape, with a thickness of $1.1 \pm 0.1 \mu\text{m}$. The length and width of the MCs are on the order of 400 and 100 μm , respectively. The ionic liquid was deposited on the cantilevers by a microspotting or painting technique. From a bulk quantity, an appropriate amount of ionic liquid was transferred onto a cantilever surface simply by touching with a thin, flexible microfiber filament. The shape and amount of the ionic liquid coatings were slightly different for each cantilever (see Fig. 2). Therefore, to minimize these differences, cantilever painting was standardized at the same location and height for each surface.

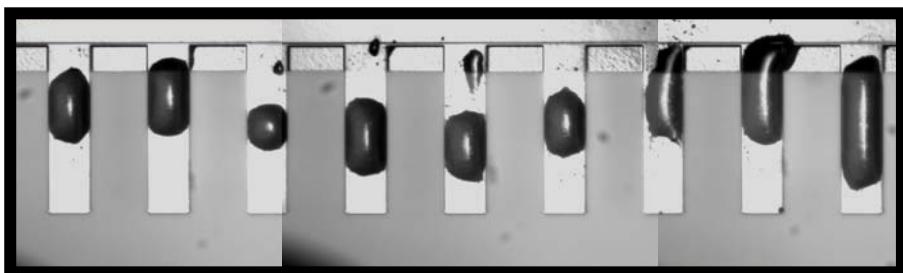


Fig. 2. Picture of ionic-liquid coated microcantilevers.

4.2 CONCENTRATION MEASUREMENTS USING IONIC-LIQUID-COATED MCs

4.2.1 Cantilever Response Measurements

Ionic-liquid-coated MCs were first used to detect water vapor, acetone vapor, and ethanol vapor in nitrogen gas flow. The vapors were produced from liquid-phase chemicals by evaporation in syringes. For this reason, chemicals of high volatility were chosen for testing the response of ionic-liquid-coated MCs.

The responses from three different cantilevers (C1, C2, and C8) were recorded for a period of 100 s each. Results in Fig. 3 show distinctive features of the responses. Measurements of the deflection of MCs show that the chemical with the highest volatility had the largest response, indicating a quantitative relationship between concentration and response. At the beginning of the response, the output signal shows an initial peak for all chemicals. Even though the initial peak is relatively small for the water-vapor output, all the signals show initial peaks that later relax to a steady-state value.

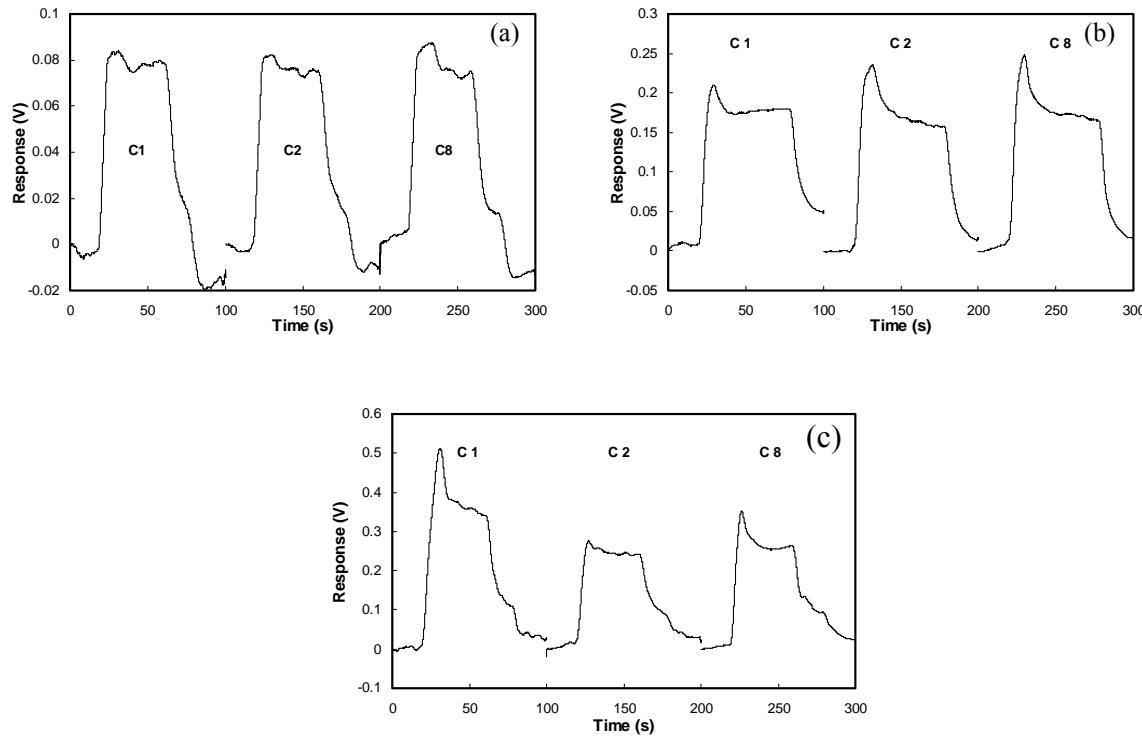


Fig. 3. Responses of cantilevers C1, C2, and C8 to vapors. Responses to (a) water vapor, (b) acetone vapor, and (c) ethanol vapor of three different cantilevers (C1, C2, and C8) with the same ionic-liquid coating. To maximize the response, it is preferable that the ionic liquid be located away from the free end of the cantilevers.

4.2.2 Reproducibility

Ionic liquids are generally known as stable chemicals with extremely low vapor pressure at room conditions. However, compared with a solid-phase coating, a liquid-phase coating might be less stable over time or to external stimuli. To ensure the stability or reproducibility of response measurements, the same response of ethanol in nitrogen was measured after a period of 3 days. During this period, the coated cantilevers were exposed to room air and temperature. The results in

Fig. 4 confirmed that no significant change in the response of the ionic-liquid-coated cantilevers occurred over a relatively long period of time.

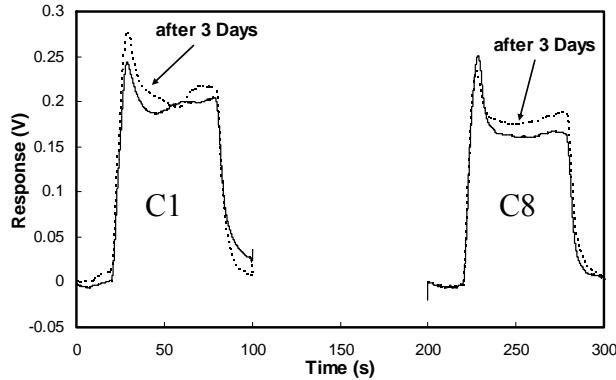


Fig. 4. Reproducibility tests for ionic-liquid-coated cantilevers with ethanol. It can be concluded that the ionic-liquid coating is stable for several days.

4.2.3 MC Surface Modification

Two approaches were used to optimize the uniformity of the ionic liquid coating on the MC surface and, consequently, the magnitude of the detection output. The first was based on mixing a nanosized powder with an ionic liquid to achieve a uniformly distributed thin coating. In this method, aluminum oxide nanopowder (40–50-nm average size) obtained from Sigma-Aldrich, St. Louis, Missouri, was mixed with ionic liquid prior to applying the coating. The aluminum oxide was not expected to react with the analytes in this study. It was also assumed that no chemical reaction occurred between the particles and ionic liquid, because the ionic liquids have been shown to be inert to other salt compounds [10]. The particles helped to increase the viscosity of the ionic liquid, which was useful in producing a thin, flat stable ionic-liquid film. A thinner coating provides a higher ratio of surface area to volume; thus, the mixing method overcame the relatively small surface stress of the smooth cantilever. The mixture did not spread well on the cantilever surface; therefore, a 10 vol % dilution of ionic liquid with 2-propanol was used instead of pure ionic liquid. When mixture of the diluted ionic liquid and powder was applied to a flat silicon plate, a thin ionic-liquid layer was evenly formed (see Fig. 5). It was assumed that the added particles would increase the total surface area of ionic liquid.

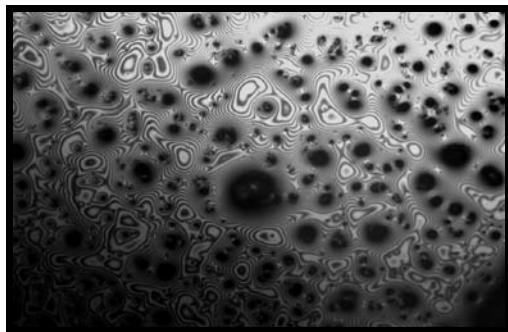


Fig. 5. Thin layer of ionic liquid on a silicon surface formed via a mixture of aluminum oxide particles and 10% ionic liquid in 2-propanol.

Three varying combinations of diluted ionic liquid and particle-mixed ionic liquid were used (Fig. 6a). One cantilever (C6) was covered with particle-mixed ionic liquid, a second (C7) was coated with particle-mixed 2-propanol and water, and a third (C8) was clean. All three cantilevers (C6, C7, and C8) were then covered with 10% diluted ionic liquid in 2-propanol. As a reference, an additional cantilever (C9) remained blank (Fig. 6b). Even though the higher-surface-area cantilevers (C6 and C7) led to a greater response with ethanol vapor, as shown in Fig. 6c, the response level was not much higher than that achieved via the MC (shown in Fig. 3) that had been coated with undiluted ionic liquid without particles. The signal from the blank MC showed noise-level fluctuation.

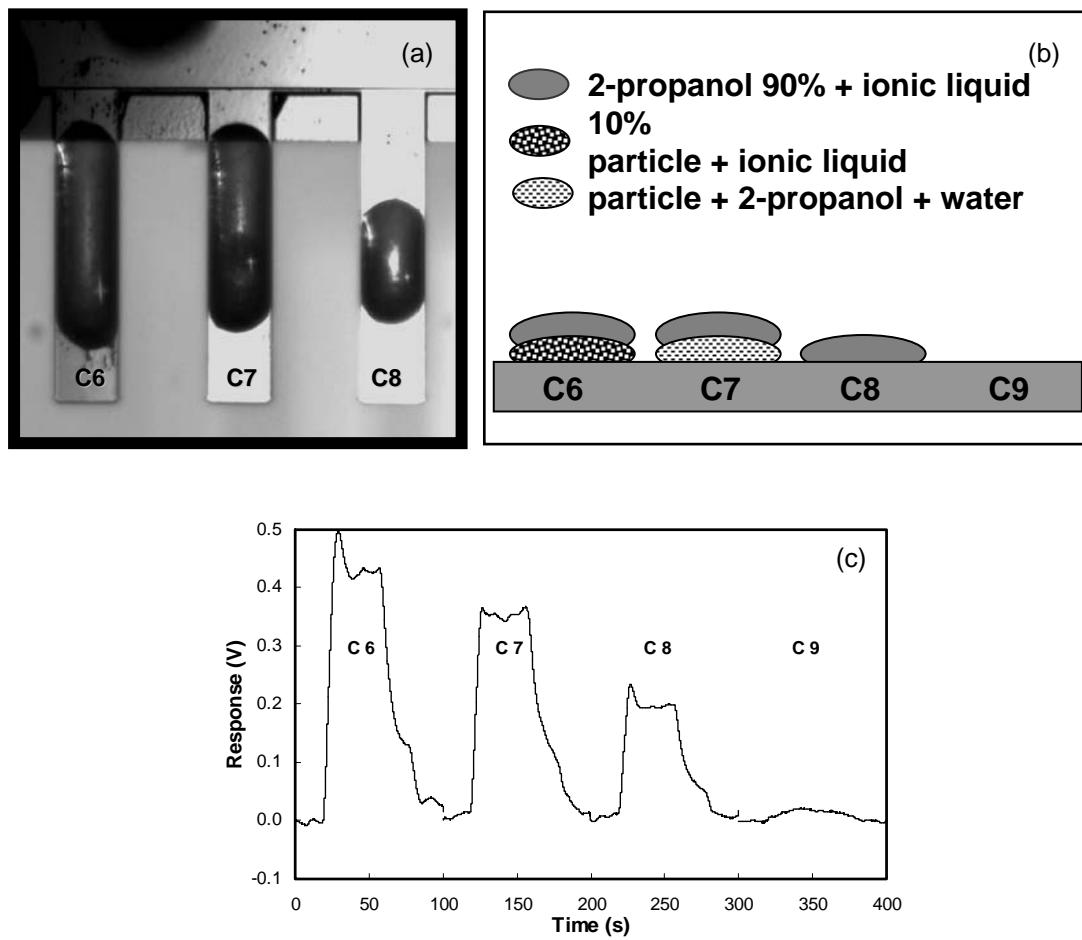


Fig. 6. Coating applications for cantilevers C6, C7, and C8, with graph showing responses of the three cantilevers to ethanol vapor. (a) Micrograph showing results of different coating applications. (b) Specific mixtures used for coating: cantilever C6, mixture of aluminum oxide particles with ionic liquid (covered with 10% dilution of ionic liquid in 2-propanol); cantilever C7, mixture of aluminum oxide particles with 2-propanol and water (covered with 10% dilution of ionic liquid in 2-propanol); cantilever C8, covered with 10% diluted ionic liquid in 2-propanol droplet (without particles); cantilever C9, blank. (c) Response of all cantilevers to ethanol vapor.

A second approach attempted to improve the detection level was the use of nanostructured cantilevers prepared by a focused ion beam. In order to increase the surface area of contact with the ionic-liquid coating, the focused ion beam was used to make grooves of controlled depth on the cantilevers. Because the cantilever surface with increased contact area holds ionic liquid more effectively, the coated ionic liquid on the grooves was expected to increase the sensitivity for detection of analytes. As shown in Fig. 7a, the ionic liquid was spread evenly on the structured MC

surface. As the number of the cantilever in the sequence increased, the grooves were made deeper (i.e., cantilever C2 had the shallowest grooves and cantilever C5 had the deepest). Cantilevers C3 and C5 were tested in terms of response to water and ethanol and showed very different responses. Fig. 7c and 7d show the responses of cantilevers C3 and C5, respectively.

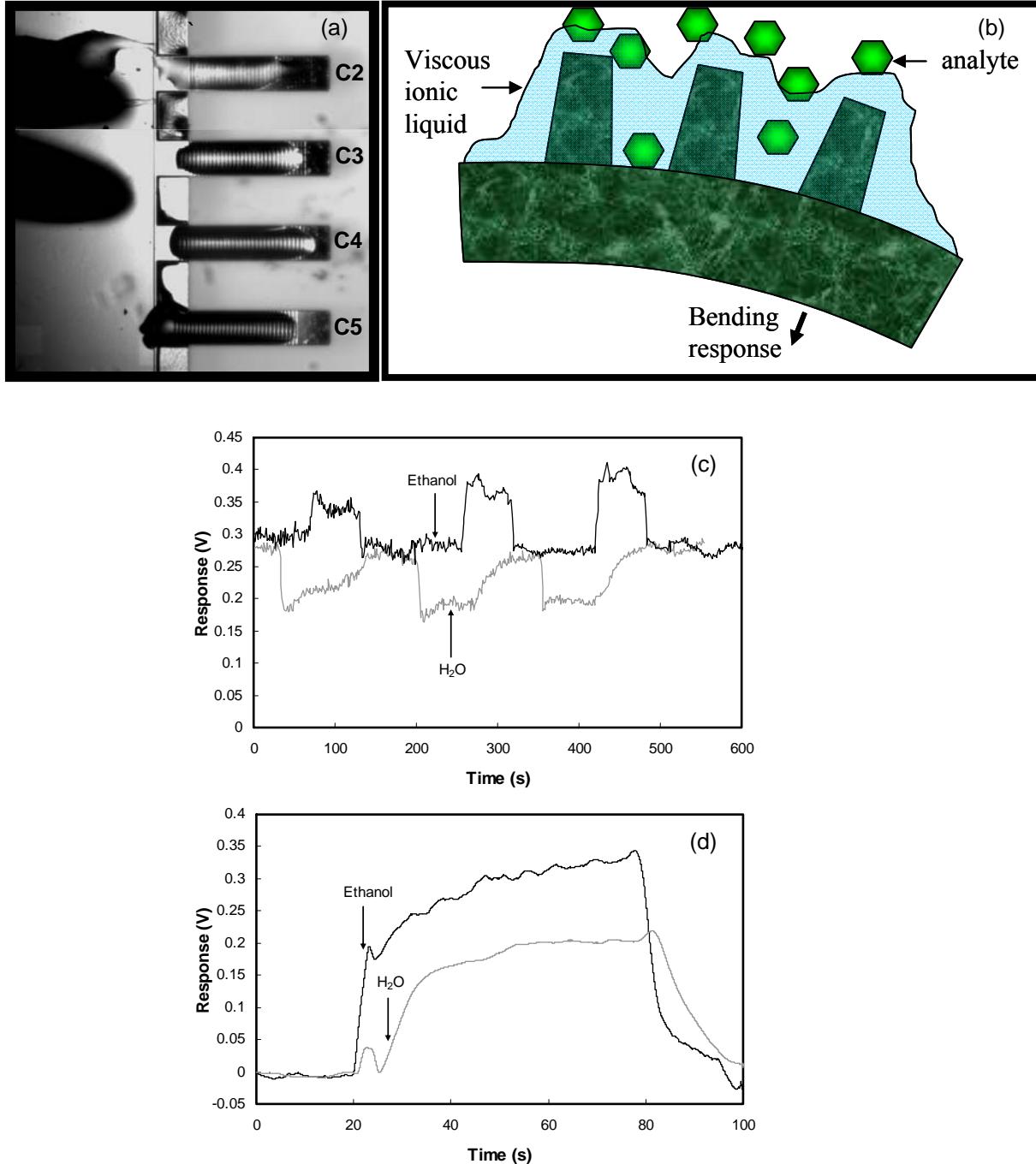


Fig. 7. Ionic-liquid coatings and bending response for microcantilevers, along with graphs showing responses of cantilevers C3 and C5 to water and ethanol vapors. (a) Micrograph showing ionic-liquid coating on structured MCs. (b) Schematic of MC bending. (c) Response of cantilever C3 to water vapor and ethanol vapor. (d) Response of cantilever C5 to water vapor and ethanol vapor.

Cantilever C3 was tested three times for each analyte and cantilever C5 was tested once. The inflow valve was opened for 1 min for each test. Before the next test, the valve was shut down for more than 1 min in order to remove the analyte residues in the flow cell. During this interval, only N₂ gas was flowing through the cell. Although a similar positive response to ethanol was detected for the two MCs, the responses to water showed opposite signals. This indicates that one response resulted from swelling—and the other, from shrinking—of the coated ionic liquid. The only difference between the two cantilevers was the depth of the grooves, those of C5 being deeper than those of C3. Despite the similar applications of the coatings of ionic liquid, this response indicates that the difference in groove depth can lead to different behavior (i.e., swelling versus shrinking) of the coatings and, thus, different responses to analytes. Swelling of the coated ionic liquid forces the cantilever to bend downward, as shown in Fig. 7b, while shrinking of the ionic liquid drives the cantilever upward.

4.2.4 Response Measurements of Cantilevers for Real Atmospheric Pollutants

The same cantilevers shown in Fig. 6a were also used for ozone detection. As shown in Fig. 8, the cantilever response to ozone (at a concentration of approximately 200 ppm) was low when compared with that for other analytes, such as ethanol. Although the response was not as strong as those of low-vapor-pressure chemicals, it had a typical initial peak and the response levels were high compared with that of the blank cantilever. The cantilever response for air was also recorded. The air-response patterns were similar to those of ozone, indicating that this particular ionic liquid may not be appropriate for ozone detection in air.

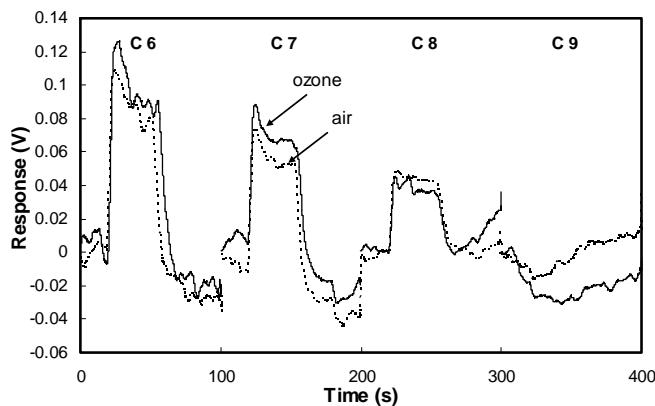


Fig. 8. Response of cantilevers C6, C7, C8, and C9 (shown in Fig. 6a) to ozone (solid line) and air (dotted line) as analytes. The similar response for the two analytes indicates that the ionic liquid used is not a good candidate for ozone detection.

The response to CO₂ was detected with a grooved cantilever (C3 in Fig. 7a). The response in Fig. 9 differs from those to the other analytes, showing a unique feature that is indicative of the affinity between the ionic liquid and the analyte. As with other analytes, a peak occurs at the first part of the injection. However, the response decreases continuously and slowly, even after the inflow valve of the analyte is shut down. Such a response indicates a high affinity between the ionic liquid and the analyte (CO₂), leading to a slow desorption after the CO₂ flow is turned off.

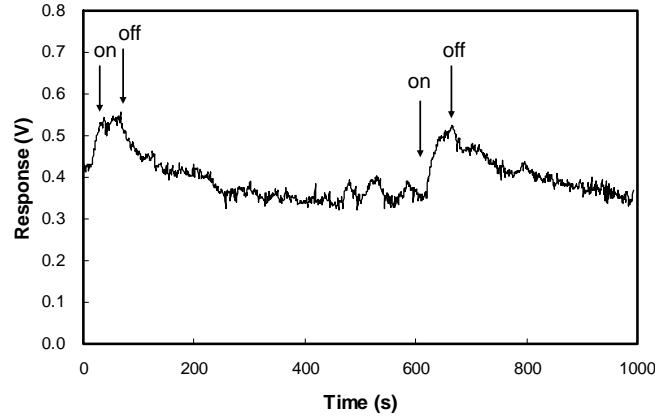


Fig. 9. Response of cantilever C3 to CO₂. The slow response after the inflow switch was turned off is a unique characteristic of the CO₂ signal.

4.2.5 Resonance-Frequency Shift

When the cantilever is considered a linear oscillator, its resonance frequency is one of the characteristics that can describe its behavior. Swelling or shrinking of the ionic liquid on the cantilever will change the resonance frequency. Therefore, the resonance-frequency shift (i.e., the change of the resonance frequency) is expected to vary for different analytes and different ionic liquids. A resonance-frequency shift, another feature that can be detected from coated MCs, was detected for both cantilevers C3 and C5, as shown in Fig. 10. The detected resonance-frequency shift varies with the type of contaminant. In Figs. 10a and 10b, the frequency shift for cantilever C3 to NO_x was greater than that for cantilever C5 to ethanol. Furthermore, the results for both cantilevers are greater than those for a blank cantilever (results not shown). When the frequency shift observed in this study for ionic-liquid-coated MCs is compared with the frequency shift observed by Baltus et al. [13] for an ionic-liquid-coated quartz crystal microbalance, the frequency shift for MCs is on the order of hundreds of hertz while that of the quartz crystal microbalance is only a few hertz. This behavior is due to the small mass of the MCs, as compared with that of the quartz crystal microbalance. Thus, the results of this study demonstrate that changes in amplitude as well as oscillation frequency shift can be measured and correlated for contaminant detection.

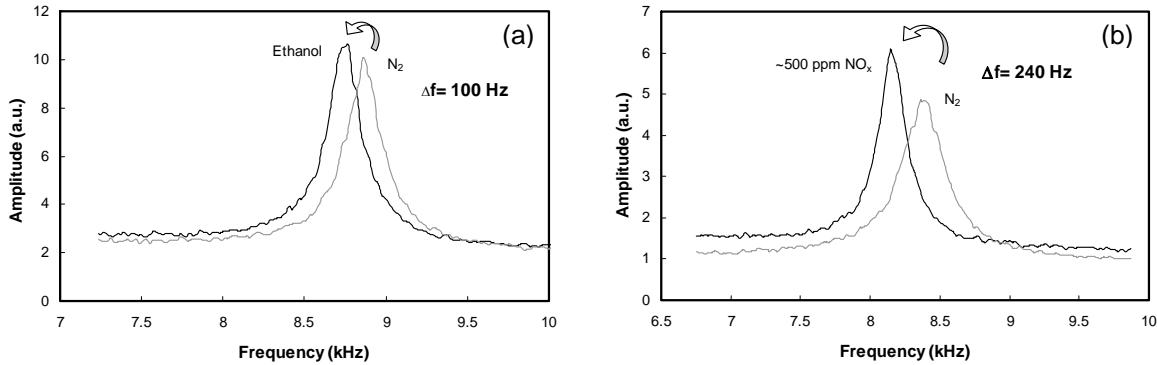


Fig. 10. Resonance-frequency shift of (a) cantilever C3 and (b) cantilever C5.

5. MEASUREMENTS OF WATER-QUALITY PARAMETERS

The response of ionic-liquid-coated cantilevers was investigated for particles suspended in water. The same hydrophobic ionic liquid used in previous experiments was also employed for this part of the work. Latex particles, with a mean diameter of $0.3\text{ }\mu\text{m}$, were suspended in water at a concentration of 100 ppm at neutral pH to minimize aggregation. As shown in Fig. 11, the submerged cantilever (in this case, cantilever 4) had a dynamic deflection response with several peaks, which represent sorption/desorption events of particles. This “noisy” behavior is unique to solids suspended in the test solution and may be used to detect the presence of particulates, including biological particles or concentration of particles of known diameter.

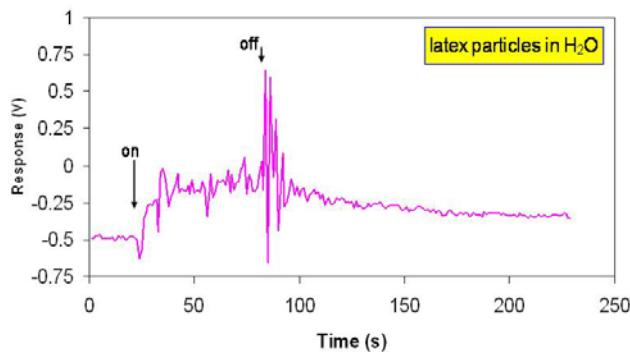


Fig. 11. Deflection response of cantilever C4 in a latex particle suspension. Particle size: $0.3\text{ }\mu\text{m}$, particle concentration: $\sim 100\text{ ppm}$.

Experiments were also conducted to measure the ionic-liquid-coated cantilever response for a solute dissolved in water. For example, the deflection response of ethanol dissolved in water is presented in Fig. 12, where the response of a coated cantilever (C4) is compared with that of a blank cantilever (C9). Both coated and noncoated cantilevers showed qualitatively a similar response. This behavior is believed to be the result of contamination on the blank cantilever. The reason is that if the blank cantilever were truly clean, it would have behaved as a symmetric cantilever—showing no response because both surfaces of the cantilever would behave the same way. It is apparent from these deflection response measurements on aqueous systems that the MC responses in condensed media are more complex than the responses of gaseous systems.

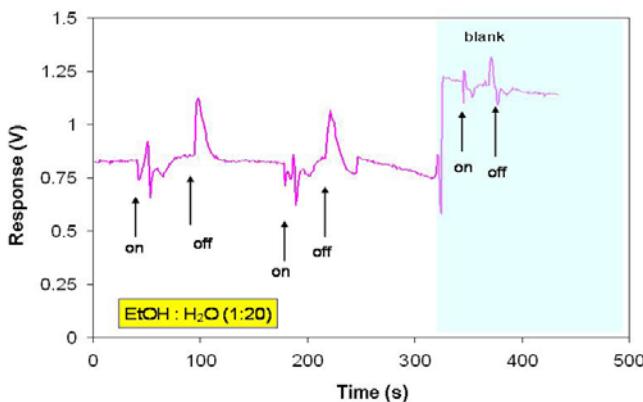


Fig. 12. Deflection response of cantilevers C4 and C9 to ethanol in water. Cantilever C4 is coated; C9 is blank.

6. MEASUREMENTS OF PARAMETERS IN EXTREME ENVIRONMENTS

The MC sensors should be able to withstand environmental extremes. In this project, high temperature was considered an extreme environment. The experimental setup for measurements at extreme environments was similar to that presented in Fig. 1, except that the system was now heated at 90°C. Both the flow cell and the stainless steel part of the gas delivery system were placed inside a thermally insulated enclosure with two heaters allowing for separate temperature control of the flow cell and the inlet tubing. The material used to build the enclosure (shroud) consisted of three layers, i.e., a layer of cotton fabric between two layers of aluminum foil. Miniature halogen quartz lamps (20 Watt) were used as heating sources that allowed us to elevate the temperature up to 100°C. Measurements of the temperature were performed using a thermocouple thermometer. A care was taken to reach a thermal equilibrium inside the enclosure and maintain the heated parts (the cell and the stainless steel part of the inlet and outlet tubing) at the same temperature. A nanostructured cantilever similar to that shown in Fig. 7a was used for these measurements. The results are presented in Fig. 13, where measurements for three different concentrations are shown at 10, 2, and 0.1% ethanol in nitrogen. It is shown that the signals from the gas phase were stable at high temperature, even at low concentrations of ethanol, up to 2%. The kinetics of responses to ethanol vapor at 90 °C (Figure 13) and ambient temperature (Figure 7d) are very similar, while the response magnitude increased slightly at the elevated temperature.

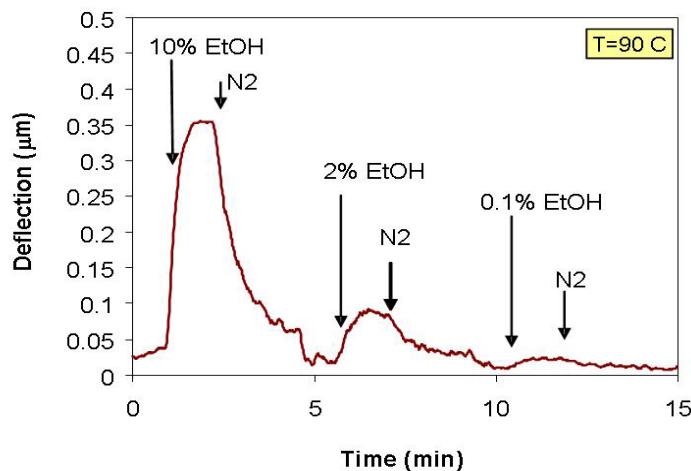


Fig. 13. Responses of a structured cantilever with an ionic-liquid coating to vapor-phase ethanol (EtOH) at an elevated temperature ($T = 90^\circ\text{C}$).

Calibration of the PSD signal performed at this stage allowed us to plot the MC response as an absolute value of the tip deflection. The calibration coefficient was found to be 0.72 μm per V.

7. FUTURE WORK

Air-quality monitoring has long been a subject of research seeking new means to observe the present conditions, as well as changes over time. Monitoring devices are needed to keep track of volatile materials used in a wide variety of remanufacturing and repair undertaken by DoD in the maintenance of its weaponry and support equipment. Fast quantification of the analyte concentrations is necessary. Integrated MEMS-based devices can be used to detect and quantify

analytes related to DoD operations. The work described in this report was focused on a concept proof of principle and has demonstrated the potential utility of ionic-liquid-coated MCs in sensors. It was found that nanostructuring of MCs can be used to help form uniform ionic liquid coatings. Further optimization of the nanostructuring techniques may be required in order to further increase response sensitivity, which in turn can be used to increase the resolution of concentration measurements. However, there is still a need to develop sensors that can be readily used in the field. This gap can be addressed in a follow-on project, where the focus will be on optimizing the materials and the packaging of the sensor. As an example, detection of nitrous oxides would assist DoD in meeting regulatory requirements and improve environmental performance. This SEED project has shown that ionic-liquid coated MCs can be used for the detection of nitrous oxides. The next step would be to conduct a systematic study with a single cantilever or array of cantilevers to correlate cantilever response with the concentration of nitrous oxides in a mixture of other analytes, including carbon dioxide and water, in air. This type of work requires additional effort in safely handling nitrous oxides, which are hazardous materials.

8. REFERENCES

1. P. G. Datskos, N. V. Lavrik, and M. J. Sepaniak, "Chemical and Biological Sensors Based on Microcantilevers," pp. 331-379 in S. Y. Yurish and M. T. S. R. Gomes, eds., *Smart Sensors and MEMS*, Kluwer Academic Publishers, The Netherlands, 2005.
2. C. Ziegler, "Cantilever-Based Biosensors," *Anal. Bioanal. Chem.*, **379**, 946-959 (2004).
3. M. Sepaniak, P. Datskos, N. Lavrik, and C. Tipple, "Microcantilever Transducers: A New Approach in Sensor Technology," *Anal. Chem.*, **74**, 568-575 (2002).
4. N. V. Lavrik, M. J. Sepaniak, and P. G. Datskos, "Cantilever Transducers as a Platform for Chemical and Biological Sensors," *Rev. Sci. Instrum.*, **75**, 2229-2253 (2004).
5. M. K. Baller, H. P. Lang, J. Fritz et al., "A Cantilever Array-Based Artificial Nose," *Ultramicroscopy*, **82**, 1-9 (2000).
6. C. A. Tipple, N. V. Lavrik, M. Culha, J. Headrick, P. Datskos, and M. J. Sepaniak, "Nanostructured Microcantilevers with Functionalized Cyclodextrin Receptor Phase: Self-Assembled Monolayers and Vapor-Deposited Films," *Anal. Chem.*, **74**, 3118-3126 (2002).
7. J. J. Headrick, M. J. Sepaniak, N. V. Lavrik, and P. G. Datskos, "Enhancing Chemical-Mechanical Transduction in Microcantilever Chemical Sensing by Surface Modification," *Ultramicroscopy*, **97**, 417-424 (2003).
8. C. D. Liang, C. Y. Yuan, R. J. Warmack, C. E. Barnes, and S. Dai, "Ionic Liquids: A New Class of Sensing Materials for Detection of Organic Vapors Based on the Use of a Quartz Crystal Microbalance," *Anal. Chem.*, **74**, 2172-2176 (2002).
9. J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, and R. D. Rogers, "Room Temperature Ionic Liquids as Novel Media for 'Clean' Liquid-Liquid Extraction," *Chem. Commun.*, **16**, 1765-1766 (1998).
10. J. McFarlane, W. B. Ridenour, H. Luo, R. D. Hunt, and D. W. DePaoli, "Room Temperature Ionic Liquids for Separating Organics from Produced Water," *Sep. Sci. Technol.*, **40**, 1245-1265 (2005).
11. S. L. I. Toh, J. McFarlane, C. Tsouris, D. W. DePaoli, H. Luo, and S. Dai, "Room Temperature Ionic Liquids in Liquid-Liquid Extraction: Effects of Solubility in Aqueous Solutions on Surface Properties," *Solvent Extr. Ion Exch.*, **24**, 33-56 (2006).
12. Q. Liao and C. L. Hussey, "Densities, Viscosities, and Conductivities of Mixtures of Benzene with the Lewis Acidic Aluminum Chloride + 1-Methyl-3-ethylimidazolium Chloride Molten Salt," *J. Chem. Eng. Data*, **41**, 1126-1130 (1996).

13. R. E. Baltus, B. H. Culbertson, S. Dai, H. Luo, and D. W. DePaoli, "Low-Pressure Solubility of Carbon Dioxide in Room-Temperature Ionic Liquids Measured with a Quartz Crystal Microbalance," *J. Phys. Chem. B*, **108**, 721-727 (2004).

Appendix. INTELLECTUAL PRODUCTS

The results of this study have been summarized in the following journal publication:

Eunhyea Chung, Nickolay Lavrik, Panos Datskos, Joanna McFarlane, Sheng Dai, and Costas Tsouris, “Microcantilever Sensors with Chemically Selective Coatings of Ionic Liquids,” *AICHE J.*, **53** (10), 2726-2731 (2007).

In addition, the results have been presented in three national and international conferences, including the SERDP workshop in 2006, as follows:

Costas Tsouris, Nickolay Lavrik, Panos Datskos, Eunhyea Chung, Joanna McFarlane, and Sheng Dai, “MEMS Sensors with Chemically Selective Coatings of Ionic Liquids,” Partners in Environmental Technology Technical Symposium & Workshop, Washington D.C., November 28-30, 2006.

Eunhyea Chung, Nickolay Lavrik, Panos Datskos, Joanna McFarlane, Sheng Dai, and Costas Tsouris, “MEMS Sensors with Chemically Selective Coatings of Ionic Liquids,” Fifteenth Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tennessee, October 21-25, 2007.

Eunhyea Chung, Nickolay Lavrik, Panos Datskos, Joanna McFarlane, Sheng Dai, and Costas Tsouris, “MEMS Sensors with Chemically Selective Coatings of Ionic Liquids,” Annual AIChE Meeting, Salt Lake City, Utah, November 4-9, 2007.

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